27. Halide Eutectic Growth

Experiment MA-131

A. S. Yue,[a†] C. W. Yeh,[a] and B. K. Yue[a]

ABSTRACT

Continuous and discontinuous lithium fluoride fibers, embedded in a sodium chloride matrix, have been produced in space and on Earth. The production of continuous fibers in a eutectic mixture was attributed to the absence of convection currents in the liquid during solidification in space. Image transmission and optical transmittance measurements of transverse sections of the space-grown and Earth-grown ingots were made with a light microscope and a spectrometer. Better optical properties were obtained from the space-grown eutectics. This result is attributed to a better alinement of lithium fluoride fibers along the growth direction.

INTRODUCTION

When certain binary eutectic mixtures solidify, one of the two phases can form fibers or platelets in a matrix of the second phase. For example, when a eutectic liquid of sodium chloride (NaCl) and sodium fluoride (NaF) solidifies, fibers of NaF (ref. 27-1) form in a matrix of NaCl. Similarly, when a liquid of NaCl and lithium fluoride (LiF) solidifies, LiF will form the fiber phase in the NaCl matrix.

Fiberlike and platelike eutectics produced on Earth are limited in quality by the presence of a banded structure (refs. 27-2 and 27-3), by discontinuity (ref. 27-4), and by faults (refs. 27-5 and 27-6) caused, at least in part, by vibration and convection currents in the melt during solidification. The presence of these defects makes the solid-state eutectic devices inefficient and useless (ref. 27-7).

If the solidification process is performed in a space environment, where there are no vibration and convection currents in the melt, there is reason to believe that continuous fiberlike eutectic microstructures can be produced. The electric, thermomagnetic, optical, and superconducting characteristics of such eutectics will be strongly anisotropic, which suggests the possibility for important applications of the eutectic devices. A Skylab experiment (ref. 27-1) of NaCl-NaF eutectic demonstrated that continuous fibers of NaF embedded in an NaCl matrix could be grown by the directional solidification technique in space.

The objectives of the Apollo-Soyuz Test Project (ASTP) MA-131 experiment were

1. To prepare, in a space environment, fiberlike LiF-NaCl eutectic with continuous LiF fibers embedded in the NaCl matrix. (This eutectic of continuous LiF fibers cannot be produced on Earth because of convection currents and vibration in the melt during solidification.)
2. To extract a few fibers from an ASTP space-grown NaCl-LiF eutectic ingot and also from Earth-grown ingots and to determine whether the extracted fibers were continuous or discontinuous.
3. To calculate the interfiber spacing of the LiF fibers.
4. To measure transmittance as a function of wavelength for the space-grown and Earth-grown ingots (both parallel and perpendicular to the fibers).

[a]University of California at Los Angeles.

[†]Principal Investigator.

EXPERIMENTAL PROCEDURE

The NaCl-29 weight percent LiF eutectic ingots were prepared from 99.96-percent-pure NaCl and 99.99-percent-pure LiF. The NaCl-LiF ingots were melted and solidified in an induction furnace having an argon atmosphere. After solidification, each ingot was machined to the shape and dimensions shown in figure 27-1 (labeled "sample").

To hold the NaCl-LiF ingot, a graphite crucible was machined from a high-purity graphite rod. Because graphite is a very fragile material, a special method was used to machine the crucibles. The graphite crucibles were calcined in vacuum at a temperature of 1223 K (950° C) for 25 hours.

The eutectic-ingot/graphite-crucible assembly was then loaded into a 304 stainless steel container of the dimensions shown in figure 27-1. The container was constructed from stainless steel tubing with a stainless steel plug heliarc-welded to one end. After the ingot-crucible assembly was loaded, the inner wall of the stainless steel container was coated with a graphite paste where the NaCl-LiF ingot was exposed to the container. A calcined graphite disk (0.025 cm (0.010 in.) thick) was then placed over the end of the ingot. The graphite paste and the disk were used to prevent a reaction between the container and the eutectic when the ingot was later remelted and resolidified. The container was then sealed by heliarc-welding a cap, with a vent hole (no. 60), in place to form the ampoule (fig. 27-1).

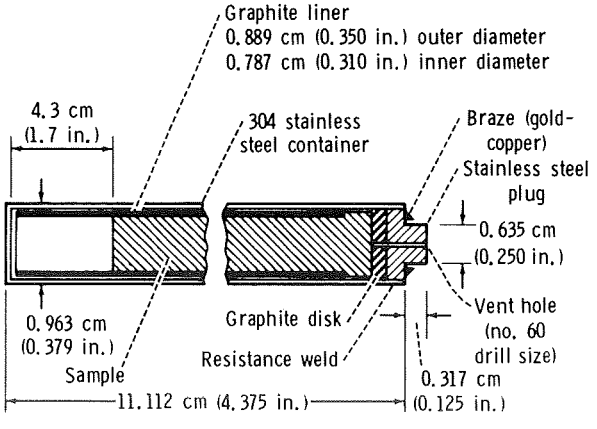

FIGURE 27-1.—Sketch of an ampoule.

Three groups of eutectic-ingot samples were used. The first (group A) was retained at the laboratory for later comparison, the second (group B) was regrown in a prototype furnace for comparison with the space-grown samples, and the third (group C) was the ASTP flight sample.

The resolidification experiment in the Apollo spacecraft was performed in the multipurpose electric furnace (ref. 27-8). A 1.3-cm (0.5 in.) portion of the eutectic ingot adjacent to the graphite disk was left unmelted; the remaining portion of the ingot was melted and resolidified unidirectionally toward the empty space of the ampoule as indicated in figure 27-1.

RESULTS

The experimental results are presented in five parts: (1) examination of the macrostructures and microstructures of the space-grown and Earth-grown eutectics, (2) extraction of continuous LiF fibers embedded in an NaCl matrix, (3) calculation of the interfiber spacing of the LiF fibers of the space-grown NaCl-LiF eutectic, (4) determination of the image transmission of space-grown and Earth-grown eutectics, and (5) determination of the optical transmittance of space-grown and Earth-grown eutectics.

Macrostructures and Microstructures

The appearance of the three ampoules after completion of the ASTP experiment is shown in figure 27-2. The surfaces of the stainless steel cylinders and plugs were in perfect condition.

The three space-grown eutectic ingots removed from the ampoules by grinding off the welded ends of each stainless steel cylinder are shown in figure 27-3. Careful inspection of the surface of the ingots revealed no evidence of reaction between the NaCl-LiF eutectic and the graphite container. In sample number 18, one transverse fracture surface occurred at the head portion (fig. 27-3(a)). However, the fracture occurred after resolidification and did not interrupt the growth pattern of the sample.

The solidified eutectic (sample no. 19) that reveals the shape of the meltback interface is shown in figure 27-4. The resolidified portion of

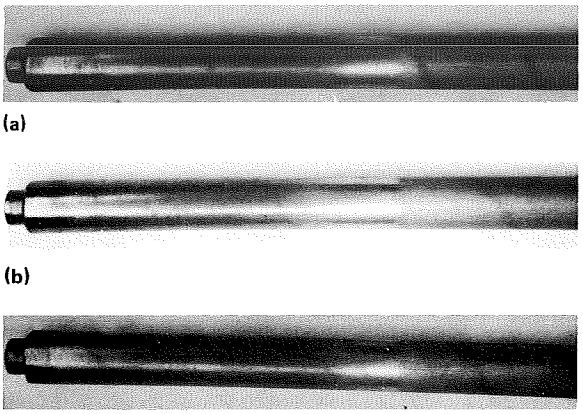

FIGURE 27-2.—Photographs of the three ASTP flight ampoules. (a) Sample number 18. (b) Sample number 19. (c) Sample number 20.

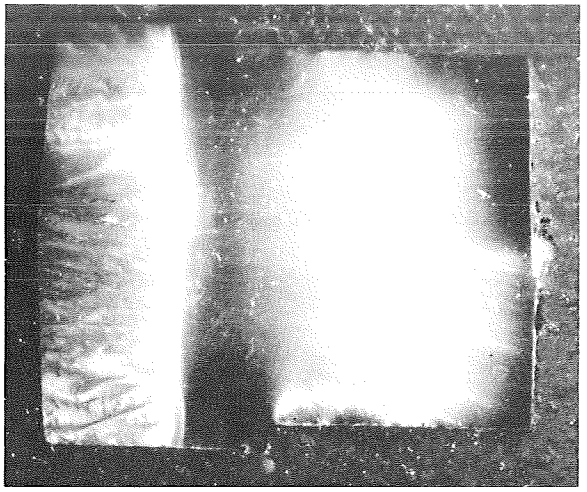

FIGURE 27-4.—Photograph showing the original shape of the solid-liquid interface of the ASTP space-grown NaCl-LiF eutectic (3.8×).

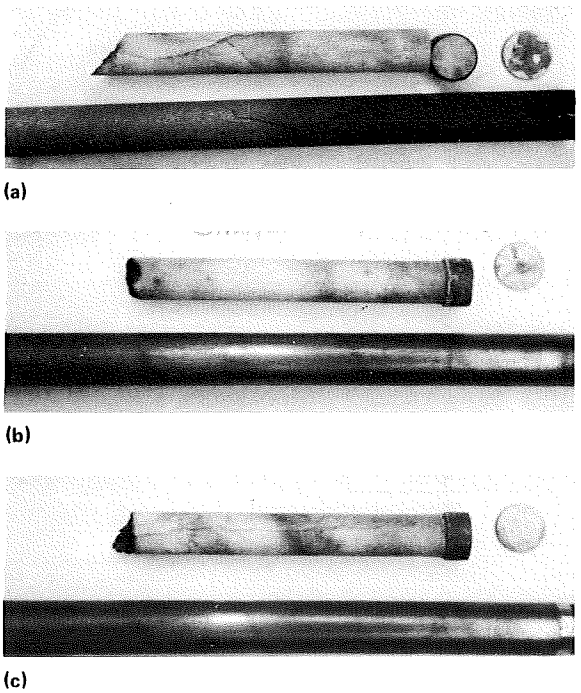

FIGURE 27-3.—Photographs of the ASTP space-grown NaCl-LiF eutectic after removal from ampoules. (a) Sample number 18. (b) Sample number 19. (c) Sample number 20.

the ingot is on the right of the interface, and the unmelted portion is on the left of the interface. In this eutectic, the remeltback interface is 0.28 cm (0.11 in.) from the left end of the ingot, whereas the same meltback distances of the other two space-grown eutectics are approximately 0.51 cm (0.20 in.). This difference may indicate a slight offset in the positioning of the heat zones in the furnace. A photomicrograph of the solid-liquid interface is shown in figure 27-5, in which the beginning of the solidification process can be seen. The elongated LiF phases (fig. 27-5) grew in a direction perpendicular to the conical solid-liquid interface; therefore, the direction of heat extraction during the onset of solidification probably was not parallel to the growth direction as intended. At a distance not far from the initial solid-liquid interface, as evidenced in figures 27-4 and 27-5, the LiF fibers began to divert toward the periphery of the ingot. Figure 27-6(a), a representative photomicrograph of a longitudinal section of space-grown sample number 19, shows the long, continuous fibers. The eutectic microstructure that resulted when the NaCl-LiF eutectic was grown on Earth in the presence of convection current is shown in figure 27-6(b); this structure reveals that the solidified LiF fibers are short and discontinuous. A representative photomicrograph of a transverse section of a space-grown eutectic is

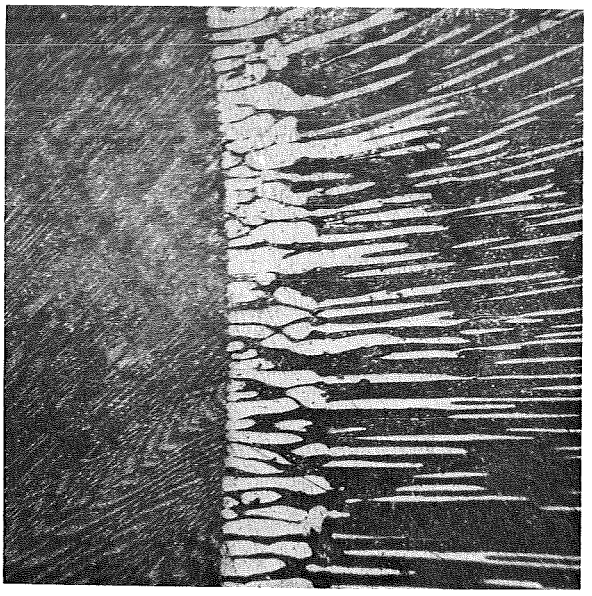

FIGURE 27-5.—Photomicrograph of the original solid-liquid interface (67×).

shown in figure 27-7, which reveals that the fibers tend to be round. Figure 27-8 is a scanning electron micrograph that shows the shapes of the Earth-grown LiF fibers. In this figure, the perspective is a view of the round LiF fibers protruding from the continuous NaCl matrix. Figure 27-9, a corresponding scanning electron micrograph of the space-grown ingot, shows that all the LiF fibers are alined unidirectionally.

Single-grain eutectic was not produced in the presence of microgravity in space. This finding is evidenced in figure 27-10, which is a transverse section of space-grown sample number 18 and shows the presence of many grains throughout the cross section. Supporting evidence is given in figure 27-11(a), which is a photograph of space-grown sample number 18. Filtered light from a microscope was directed at the lower end of the eutectic. Good alinement of LiF fibers along the longitudinal axis permitted transmission of light from the lower end and propagation through the ingot for a longer distance with a much stronger intensity than with the Earth-grown ingot (fig. 27-11(b)). Light was not transmitted through the upper portion of the space-grown eutectic because, in that portion of the ingot, the fibers were not alined with the longitudinal axis.

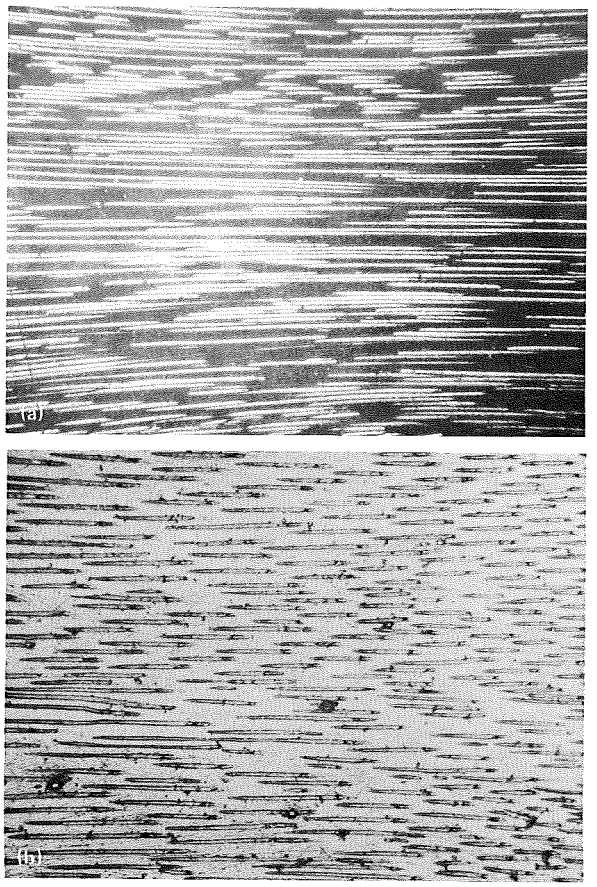

FIGURE 27-6.—Photomicrographs of a longitudinal section of the NaCl-LiF eutectic. (a) Space-grown eutectic (sample no. 19) showing continuous LiF fibers (30.5×). (b) Earth-grown eutectic showing discontinuous LiF fibers (115.5×).

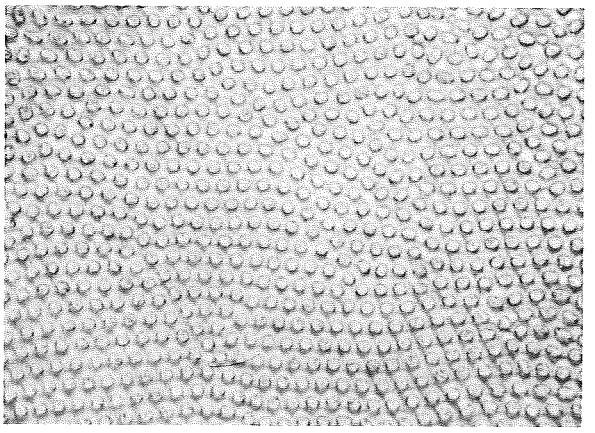

FIGURE 27-7.—Photomicrograph of the transverse section of an ASTP space-grown eutectic showing the round shapes of LiF fibers (205×).

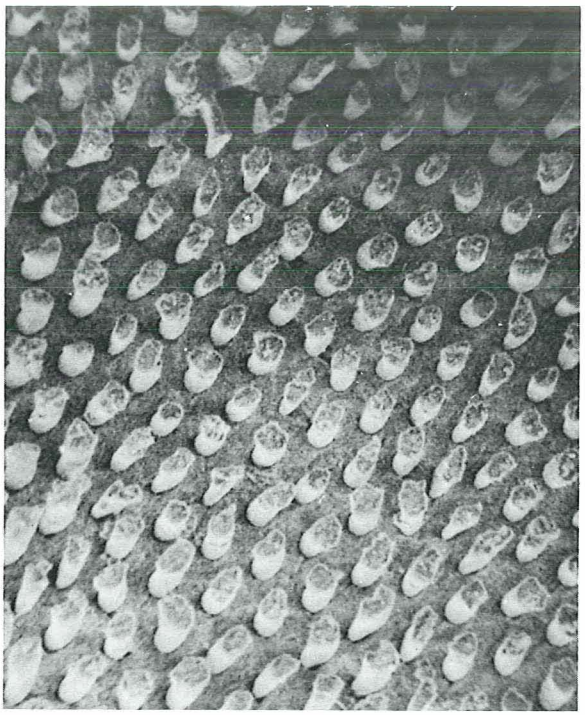

FIGURE 27-8.—Scanning electron micrograph of the Earth-grown LiF fibers (1058×).

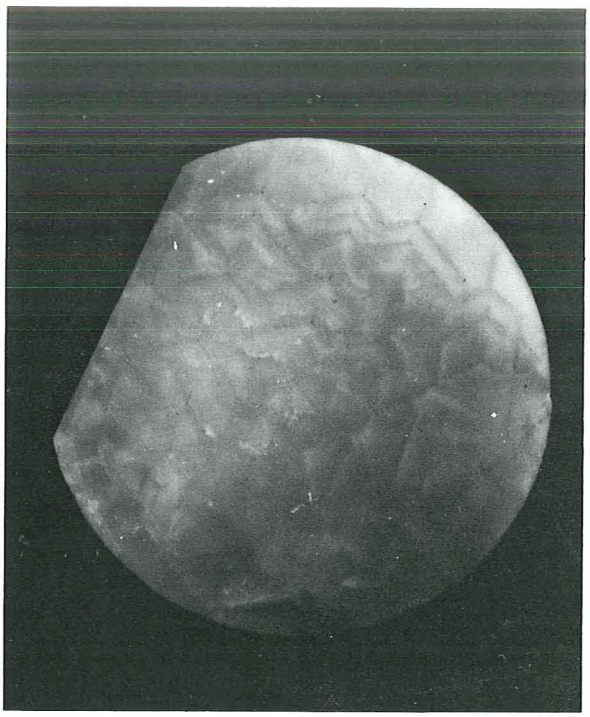

FIGURE 27-10.—Photograph of the transverse section of the NaCl-LiF eutectic showing grains and subgrains (sample no. 18, 7.9×).

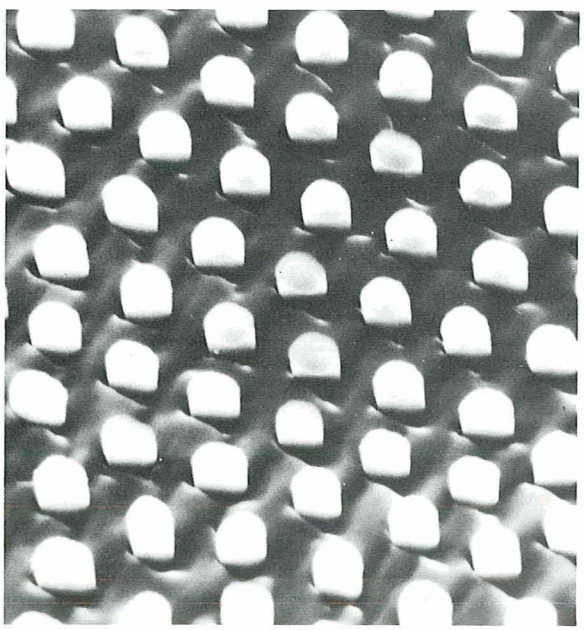

FIGURE 27-9.—Scanning electron micrograph of the ASTP space-grown LiF fibers (1900×).

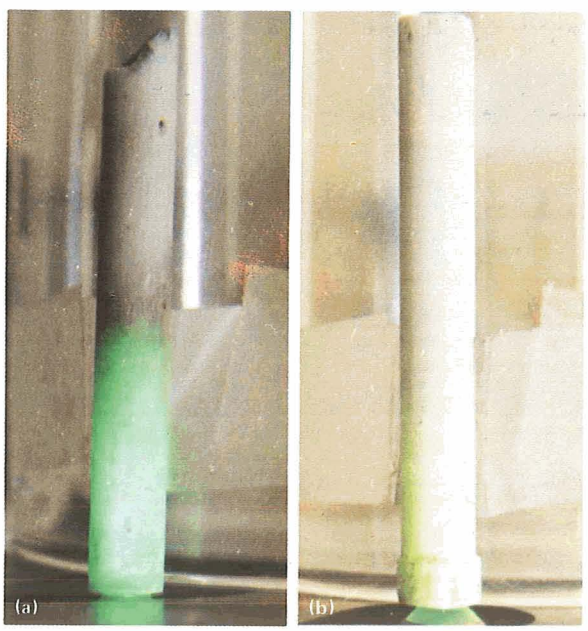

FIGURE 27-11.—Photographs of NaCl-LiF eutectics. (a) ASTP space grown (sample no. 18). (b) Earth grown.

Lithium Fluoride Fibers

Figure 27-12(a) is a photograph of a space-grown ingot that was taken when the LiF fibers were suspended in methyl alcohol. From this figure, it is evident that the LiF fibers are continuous and straight. When an Earth-grown NaCl-LiF eutectic ingot (from group A) was immersed in the same solution, LiF fibers could also be extracted from the NaCl matrix. However, as indicated in figure 27-12(b), the extracted fibers were short and discontinuous, which is in agreement with prediction. Based on this analysis, it was tentatively concluded that continuous LiF fibers were produced in space.

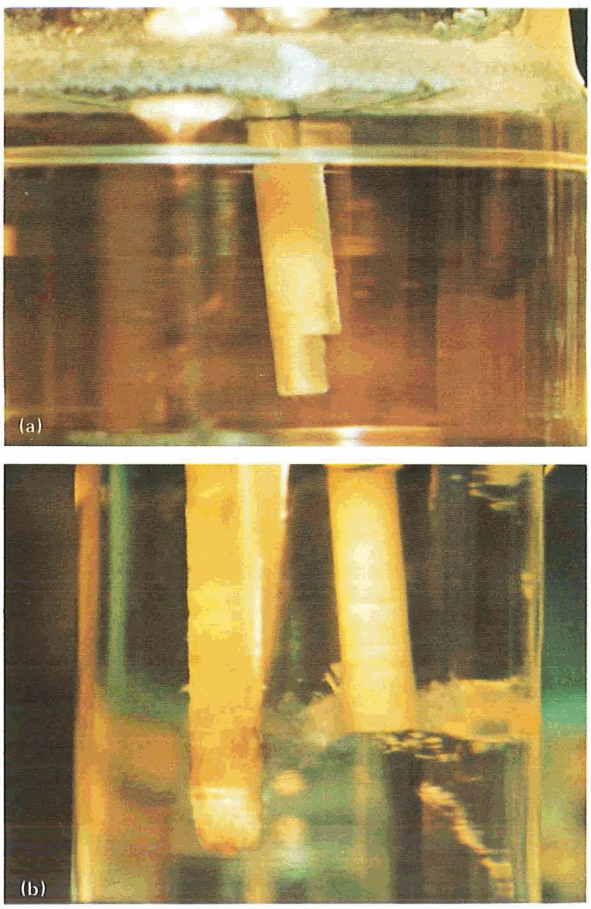

FIGURE 27-12.—Photographs of NaCl-LiF eutectic ingot (2×). (a) ASTP space-grown ingot showing continuous LiF fibers. (b) Earth-grown ingot showing discontinuous and randomly oriented fibers.

Interfiber Spacing

The measured interfiber distances in space-grown, prototype-furnace-grown, and Earth-grown ingots, at growth rates of approximately 4.5 μm/sec, are listed in table 27-I. The average fiber diameter of the prototype-furnace-grown and space-grown ingots is 3.6 μm. These measurements indicate no significant difference in interfiber spacing between the space-grown and the prototype-furnace-grown ingots. The interfiber spacing of the Earth-grown eutectic is smaller than that of the space-grown eutectic because the Earth-grown eutectic was subjected to a faster cooling rate during growth.

TABLE 27-I.—Measured Interfiber Distances[a] of Eutectic Ingots

Sample no.	*Interfiber distance, μm*
ASTP space grown	
18	6.68
19	6.41
20	5.41
Prototype furnace grown	
1	6.92
2	7.35
3	6.70
Earth grown	
Laboratory sample	4.5

[a]Growth rates of approximately 4.5 μm/sec.

Image Transmission

Image transmission properties similar to those of fiber optic materials were obtained with an Earth-grown NaCl-NaF eutectic (ref. 27-9). Because the eutectic in the referenced case had discontinuous NaF fibers, far better results were expected to be obtained if a similar halide eutectic having continuous fibers was produced in space. Two 2-mm-long cylindrical sections were cut from space-grown (group C) and Earth-grown (group A) NaCl-LiF eutectic ingots. Image transmission experiments were performed on these two sections, and the results are shown in figure 27-13. Figure 27-13(a) shows that an image was transmitted from a source (a sheet of paper containing the word "solar") through the length of the sample (2 mm) to its surface. The transmitted image has the same dimensions as the source, an indication that the LiF fibers are perpendicular to the plane of the paper. However, the transmitted image is not as clear as the original image of the source; therefore, a loss of light through transmission is indicated. Some loss is common to all fiber optic materials (ref. 27-10). An image transmitted through a section of an Earth-grown eutectic was also observed as seen in figure 27-13(b). However, the image is unclear and the dimensions of the letters "S" and "E" are larger than those of the source, an indication that the fibers are diverged away from the source.

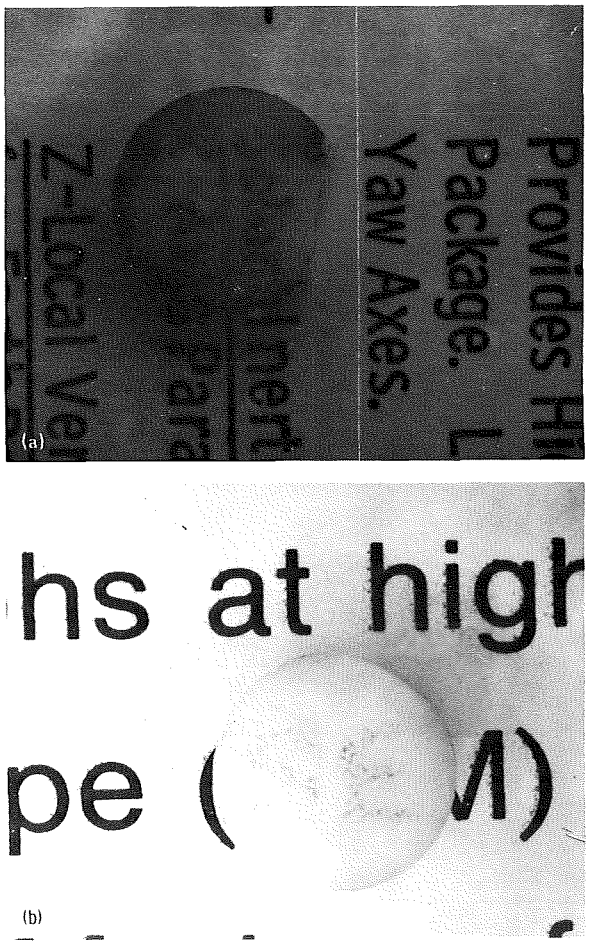

FIGURE 27-13.—Image transmission macrograph of NaCl-LiF eutectics (sample thickness, 2 mm; 3.8×). (a) ASTP space grown. (b) Earth grown.

Optical Property

In a previous ground-based study (ref. 27-9), an NaCl-NaF eutectic was found to be a far-field infrared transmitting medium for wavelengths longer than the interfiber distance. Because the NaCl-NaF eutectic used for optical measurement had discontinuous NaF fibers embedded in an NaCl matrix, better results were expected if continuous fibers were obtained. This was indeed the case, as demonstrated in the Skylab experiment (ref. 27-1). Similar experiments comparing transmission properties of space-grown and Earth-grown NaCl-LiF eutectics were conducted for ASTP. A comparison of the far-field infrared transmission of transverse sections of three NaCl-LiF eutectic samples is shown in figure 27-14. The ASTP space-grown eutectic is shown to have the highest transmittance over nearly the entire wavelength range, an indication that it had the highest percentage of fibers parallel to the growth direction. The transmittance result also shows that, over part of the wavelength range, the prototype-furnace-grown eutectic had a lower transmittance than the laboratory-grown eutectic.

The effect of section thickness on transmission for the prototype-furnace-grown eutectics and the ASTP space-grown eutectics is shown in figure 27-15. In both cases, the thinner the section, the higher the transmittance for a fixed wavelength. This observation is in agreement with absorption laws as expected.

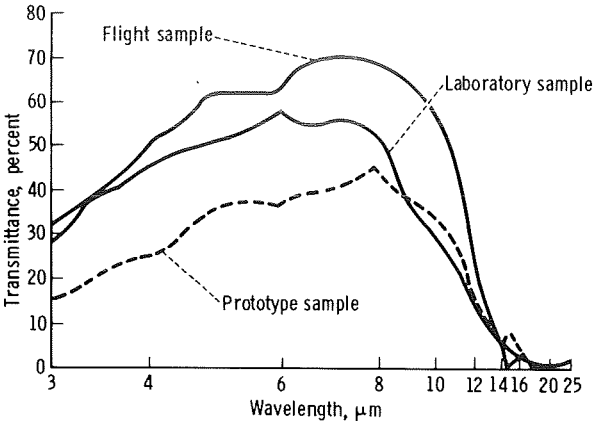

FIGURE 27-14.—Far-field infrared transmission curves of transverse sections of NaCl-LiF eutectics grown on Earth and in space. The sample thickness was 0.0536 cm (0.0211 in.).

Figures 27-16(a) and 27-16(b) show plots of transmittance as a function of wavelength for a longitudinal section of a laboratory-grown eutectic (group A), using polarized light and with the electric field **E** parallel and perpendicular to the fiber axes, respectively. Figures 27-17(a) and 27-17(b) show the same curves for the space-grown eutectic (sample no. 18). For both orientations, the transmittance for the space-grown eutectics is lower than it is for the Earth-grown eutectics over the range of wavelengths measured. It is difficult to explain this peculiar phenomenon at the present time.

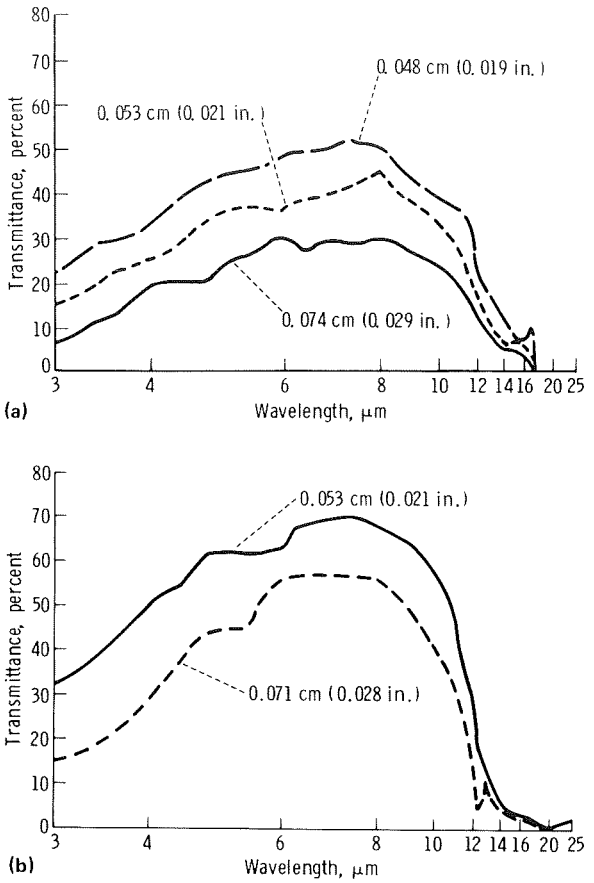

FIGURE 27-15.—Far-field infrared transmission curves of transverse sections of NaCl-LiF eutectics having different thicknesses. (a) Prototype-furnace-grown eutectic. (b) ASTP space-grown eutectic.

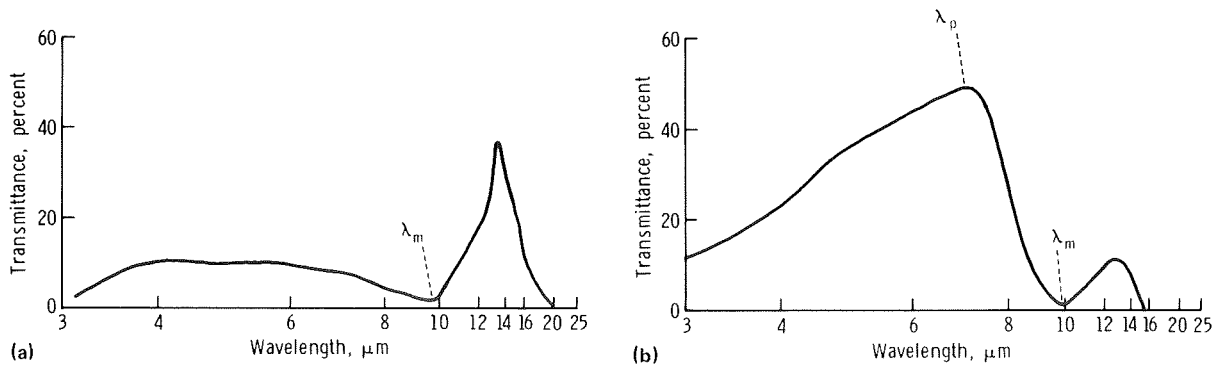

FIGURE 27-16.—Far-infrared transmittance curves of a longitudinal section of a laboratory-grown NaCl-LiF eutectic (group A). (a) $\mathbf{E}_{\parallel}$ fiber axis; λ_m is the maximum wavelength. (b) $\mathbf{E}_{\perp}$ fiber axis; λ_p is the peak wavelength.

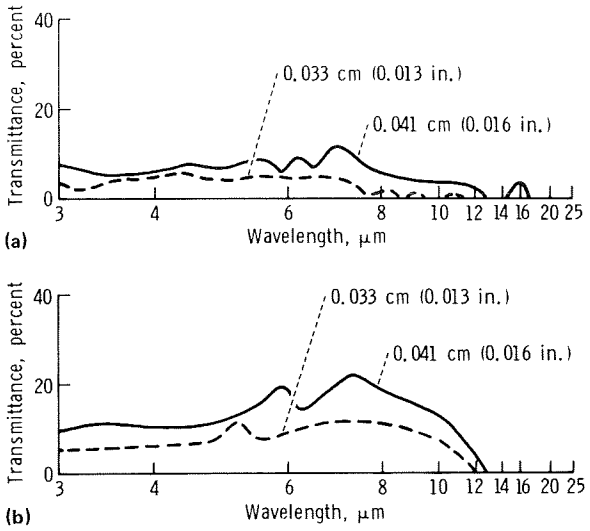

FIGURE 27-17.—Far-infrared transmittance curves of a longitudinal section of the ASTP space-grown NaCl-LiF eutectic of varying thicknesses. (a) $\mathbf{E}_{\parallel}$ fiber axis. (b) $\mathbf{E}_{\perp}$ fiber axis.

DISCUSSION

Lithium Fluoride Fibers

In a zero-g environment, there is no gravity-driven convection current in the liquid during solidification, and there is no difficulty in mixing two liquid phases of different densities. Furthermore, vibration levels in the spacecraft are far lower than those on Earth. Consequently, a homogeneous eutectic mixture consisting of continuous fibers can be produced in a space environment, and microstructure (which is sensitive to convection currents and vibration) can develop undisturbed. Accordingly, the success in producing continuous LiF fibers, as evidenced in figure 27-12, is due mainly to the absence of convection current in the melt during resolidification in space.

Optical Property

Pure NaCl and NaF crystals have approximately 95 percent transmittance per centimeter of thickness up to 15 and 9 μm, respectively, in the far-infrared wavelength region (ref. 27-1). Beyond these wavelength ranges, these crystals have zero transmittance because of the optical modes of lattice vibration of ionic crystals. If a thin piece of NaCl-LiF eutectic is cut along its fiber axis (longitudinal section), as illustrated in figure 27-18, and is measured in the 2- to 20-μm wavelength region with an infrared spectrometer, typical "transmittance as a function of wavelength" curves with polarized beam parallel and perpendicular to fiber axes are the result (figs. 27-16(a) and 27-16(b), respectively). For the electric field parallel to the fiber axes, the transmittance is near zero over a range of wavelengths for which the maximum wavelength λ_m is less than 10 μm. When the electric field is perpendicular to the fiber axes, the percentage of transmittance increases over a range of wavelengths less than λ_m and reaches a maximum value at a wavelength of 7.2 μm, which is designated a peak wavelength λ_p as indicated in figure 27-16(b). Because a thin NaCl-LiF eutectic sheet has these characteristics, it can be used as a polarizer and a modulator. It can transmit or block light rays at a specified wavelength when the electric field is rotating. The investigators have advanced an explanation that accounts for this phenomenon in terms of two-dimensional Bragg scattering and the polarization effect of Rayleigh scattering.

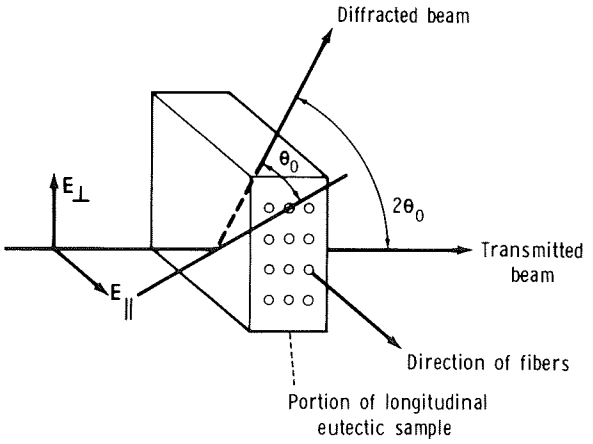

FIGURE 27-18.—Diagram illustrating factors involved in analyzing scattering measurements for transmission through a longitudinal sample section.

SUMMARY

The following conclusions can be drawn from this investigation.

1. Continuous LiF fibers, regularly arranged in a portion of the NaCl matrix that has been resolidified unidirectionally in a space environment, have been produced.

2. Larger transmittance over a wider wavelength and better image transmission were obtained for transverse sections of the space-grown eutectic ingots.

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